PCCP

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Z. Li, M. Jibran, X. Sun, A. Pratt, B. Wang, Y. Yamauchi and Z. Ding, *Phys. Chem. Chem. Phys.*, 2018, DOI: 10.1039/C8CP02361A.

View Article Online
DOI: 10.1039/C8CP02361A

Enhancement of the spin polarization of an Fe_3O_4(100) surface by nitric oxide adsorption

Z.Y. Li[1], M. Jibran[1], X. Sun[1,2]*, A. Pratt,[2,3] B. Wang[1], Y. Yamauchi[2] and Z.J. Ding[1]

1. Key Laboratory of Strongly-Coupled Quantum Matter Physics, Chinese Academy of Sciences, and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

2. National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047,Japan

3. Department of Physics, University of York, Heslington, York YO10 5DD, UK

*Email: sunx@ustc.edu.cn

Abstract

The geometric, electronic and magnetic properties of a nitric oxide (NO) adsorbed Fe_3O_4(100) surface have been investigated using density functional theory (DFT) calculations. NO molecules preferentially bond with surface Fe(B) atoms via their N atoms. The generalized gradient approximation (GGA) is not recommended to be used in such a strongly correlated system since it provides not only an overestimation of the adsorption energy and an underestimation of the Fe(B)-N bond length, but also a magnetic quench of the adsorbate and the bonded Fe(B) atoms. In contrast, a tilted geometry and a magnetization of the adsorbate and the bonded Fe(B) atom are obtained after including the strong on-site Coulomb interactions through a Hubbard term (GGA+U). The spin-down $2\pi^*$ states of the NO molecule are filled and broadened due to the adsorbate-substrate interaction and the molecule-molecule interaction. The surface spin polarization close to the Fermi level is expected to be greatly enhanced by the NO adsorption which has significance for interface design in spintronic devices.

View Article Online
DOI: 10.1039/C8CP02361A

I. Introduction

Magnetite Fe_3O_4 has attracted much attention as a potential material for spintronic devices due to the predicted half-metallic behavior in its bulk together with its high Curie temperature.[1] However, a significant reduction in the spin polarization at the Fermi level (P_{EF}) is observed at the surface of Fe_3O_4 with P_{EF} values of only (-55±10)% and -40% measured for the Fe_3O_4(100) orientation at room temperature using spin-resolved photoemission spectroscopy (SPPES).[2,3] Furthermore, using the extremely surface sensitive technique of spin polarized metastable de-excitation spectroscopy, the spin asymmetry at the Fe_3O_4(100) surface was determined to be only 5%.[4,5] Density functional theory (DFT) calculations indicate that this large reduction in P_{EF} from the half-metal value of 100% is mainly caused by surface electronic states due to the O and Fe(B) atoms at the topmost reconstructed layer. [6,7]

Efforts have been made to improve the P_{EF} through surface modification with a significant enhancement observed for the H-adsorbed Fe_3O_4(100) surface using both SPMDS and SPPES and successfully explained through DFT calculations.[4,6,8] However, the electronic states with -100% spin-polarization are localized at surface Fe(B) atoms and do not extend to surface O atoms or adsorbed H atoms.[6] Our recent calculations predict that half-metallicity can also be recovered for the Fe_3O_4(100) surface through C or B adsorption with a considerable presence of -100% spin-polarized states at the adsorbate.[9,10] To deposit atomic C or B though, very high temperatures are required making the preparation of this system difficult.

View Article Online
DOI: 10.1039/C8CP02361A

The above previous studies focus on surface modification of Fe_3O_4 through the adsorption of atomic species (H, C, B) which form strong bonds with O atoms thereby quenching oxygen dangling bonds at the surface. Here, we adopt a different approach by investigating surface modification of $Fe_3O_4(100)$ through molecular adsorption which is usually much easier to realize experimentally than atomic adsorption. Nitric oxide (NO) is selected due to the fact that it has an unpaired electron at the Fermi level. Our calculation predicts that the Fe(B) atoms at the surface bond with the adsorbed NO molecules and are therefore no longer directly exposed to the vacuum. Adsorption induces the filling of the spin-down $2\pi^*$ states of NO molecules and the surface spin polarization is predicted to be significantly enhanced.

II. Calculation Methods

All calculations were performed within the framework of DFT using a plane-wave basis set, as implemented in the Vienna *ab initio* simulation package (VASP).[11,12] Electronic exchange correlation interactions are described by the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form.[13] The projector-augment wave method is used to represent the electron-ion interactions.[14,15] The Hubbard parameter (U) is introduced for Fe 3*d* electrons to describe the on-site Coulomb interaction.[16] Different effective U values from 0 to 5 eV are used to investigate the influence of the strong electron correlation in this system. The Brillouin-zone integration is calculated with a 4×4×1 *k*-point grid using the Monkhorst-Pack method.[17] All calculations are spin-polarized with a 400 eV plane-wave energy cutoff.

View Article Online
DOI: 10.1039/C8CP02361A

A reconstructed substrate is used with a $(\sqrt{2}\times\sqrt{2})R45^{\circ}$ unit cell, which has been observed by low energy electron diffraction (LEED)[2,7] as well as by scanning tunneling microscopy (STM)[18] and reported by DFT calculations.[2,7,19] The surface is reproduced by a 13-layer slab with both sides terminated by octahedral Fe(B) atoms, which is energetically more favorable than a surface terminated by tetrahedral Fe(A) atoms.[20,21] The vacuum region is as large as 17.5 Å. NO molecules are adsorbed onto both the top-most and bottom-most surfaces. All atoms are relaxed until the force on each atom is less than 0.01 eV $Å^{-1}$.

III. Results and Discussion

There are two kinds of O atoms on the Fe(B)-terminated $Fe_3O_4(100)$ surface, denoted by O1 (without an Fe(A) neighbor) and O2 (with an Fe(A) neighbor), as shown in Fig. 1. Three adsorption sites, Fe(B), O1 and O2, are investigated with either the N or O terminal directed towards vacuum. The adsorption energy (Fig. 1) is defined as $E_{ads}=\left(E_{NO/Fe_3O_4}-E_{Fe_3O_4}-nE_{NO}\right)/n$, where E_{NO/Fe_3O_4}, $E_{Fe_3O_4}$ and E_{NO} are the total energies of the NO-adsorbed $Fe_3O_4(100)$ surface, the clean $Fe_3O_4(100)$ surface and a single NO molecule, respectively. *n* equals eight since each surface side has four adsorbed NO molecules. Both GGA and GGA+U (for all non-zero values of U_{eff}) predict that the Fe(B) is the most energetically favorable site with the O-terminal towards the vacuum. This is markedly different to previous studies investigating the adsorption of atomic H, B, and C in which O1 was determined to be the most energetically preferred site.[6,9,10] NO molecules that approach a surface via the N terminal to bond with metallic atoms have also been observed for $CuFe_2O_4(100)$,

View Article Online
DOI: 10.1039/C8CP02361A

$ZnGaAlO_4$(100) and NiO(100) substrates.[22-24]

Fig. 1 shows a large difference in the adsorption energy of NO molecules on the Fe(B) site for the GGA (-1.385 eV) and GGA+U (-0.823 eV with U_{eff}=3.8 eV) calculations indicating the significant effect of strong electron correlation. An upright configuration is obtained using GGA with a short bond length of Fe(B)-N (1.635 Å). In contrast, a tilted configuration is achieved using GGA+U with a longer bond length of Fe(B)-N (2.081 Å). To investigate in detail the strong electron correlation effect, calculations were performed with different U_{eff} values (0~5.0 eV). As indicated in Fig 2(a), the adsorbed NO molecule maintains an upright configuration ($\alpha_{O\text{-}N\text{-}Fe(B)}$=180^o) and a short bond length ($d_{Fe(B)\text{-}N}$) only when U_{eff} is very small (≤ 0.5 eV). The adsorbed NO molecule becomes tilted when U_{eff} is larger than 0.5 eV with the Fe(B)-N bond elongating at the same time. It is worth noting that the almost linear variation of the tilting angle $\alpha_{O\text{-}N\text{-}Fe(B)}$ and the bond length $d_{Fe(B)\text{-}N}$ are very slight when U_{eff} is larger than 1.5 eV. It has been demonstrated that NO adsorbs via the N atom on top of a Ni atom of the NiO(100) surface with a tilted geometry using near-edge X-ray adsorption fine structure (NEXAFS)[25] and photoelectron diffraction (PED)[26-28] experiments. The overestimation of the adsorption energy and underestimation of the adsorbate-substrate bond length have also been obtained for the NO-adsorbed NiO(100) surface through GGA calculation.[24] The adsorption energy of a NO molecule on the NiO(100) surface is 1.24 eV through GGA and 0.40 eV through GGA+U. The latter is much closer to the experimental value (0.57 eV)[29] indicating that electron correlation should certainly be included in such systems.[24]

View Article Online
DOI: 10.1039/C8CP02361A

Electron correlation effects also influence the magnetic properties of the adsorbate and the substrate. The adsorbed NO molecules and the NO-attached Fe(B) atoms are completely demagnetized when the value of U_{eff} is very small (≤ 0.5 eV) (Fig. 2b). In contrast, the magnetic moment of Fe(B) increases abruptly at 1.0 eV of U_{eff} and is very close to the moment of Fe(B) at the clean Fe_3O_4(100) surface when U_{eff} is larger than 1.5 eV. The adsorbed NO molecules also show magnetization at $U_{eff} > 0.5$ eV. Compared to a free NO molecule, the absolute value of the magnetic moment of the N atom (m_N) is reduced by ~0.08 μ_B but the moment of the O atom is enhanced by ~0.14 μ_B. A magnetic quench is also obtained in GGA calculations for the NO-adsorbed NiO(100)[24] and MnPc[30] surfaces.

It is not recommended to use GGA for such strong correlated systems, considering the obvious misrepresentation of the band-gap and the geometric, electronic, and magnetic properties.[24,30] On the other hand, GGA+U (with an appropriate value of U_{eff}) is a reliable method and can be applied to strongly correlated systems with many atoms, in comparison with the method of time-consuming hybrid functionals. In the following text, we discuss results calculated using the GGA+U method. Most DFT-based investigations of Fe_3O_4 use a U_{eff} of about 3.6 to 4.0 eV according to the comparison of the calculated band gap of bulk Fe_3O_4 with the experimental one. The average value of 3.8 eV for U_{eff} is adopted in this study.

Fig. 3a shows the spin-resolved band structure and the total density of states (DOS) of the Fe_3O_4(100) surface. There are eight spin-up surface-state bands (SSB) slightly below the Fermi level for the clean surface (blue lines in left panel of Fig. 3a),

View Article Online
DOI: 10.1039/C8CP02361A

resulting in a considerable spin-up DOS (right panel of Fig. 3a). These spin-up SSB are mainly contributed to by the d_{x2-y2} orbital of Fe(B) atoms as well as the *p* orbital of O1 and O2 atoms at the topmost layer (Supplementary Material). Although there are several spin-down bands just below the Fermi level (magenta lines in the middle panel of Fig. 3a), they are dominated by contributions from *d* orbitals of Fe(B) atoms in deeper layers with only very a slight contribution from surface Fe(B) atoms (Supplementary Material). The existence of spin-up SSB induces a low surface spin polarization, which is consistent with the small value of the spin asymmetry observed in our previous experiments.[4,5]

After the adsorption of NO molecules, the spin-up SSB with surface Fe(B), O1 and O2 atoms contributing most strongly (blue lines in left panel of Fig. 3b). However, the energy levels of the SSB are shifted to deeper levels by approximately 0.23 eV (at the Γ point). Therefore, no spin-up DOS exists in the energy range of -0.34 eV to E_F for the NO-adsorbed Fe_3O_4(100) surface. For the spin-down band structure, the valence bands energies are also shifted to a deeper level due to the adsorption of NO (magenta lines in middle panel of Fig. 3b). Another remarkable phenomenon is that eight new bands appear just below the Fermi level (green lines in middle panel of Fig. 3b). The band-decomposed charge density shows that half of the new spin-down bands are mainly composed of *p* orbital states of the adsorbed NO molecules (top panel of Fig. 3c) with minor contributions from the d_{x2-y2} orbital of Fe(B) atoms and the *p* orbital of O2 atoms. The molecule-molecule interaction can be observed in this charge density map. The charge density of the other half bands (bottom panel of Fig. 3c) indicates an

View Article Online
DOI: 10.1039/C8CP02361A

obvious hybridization between the *p* orbital of the N atom in NO and the d_{z2} orbital of the substrate Fe(B) atoms.

After adsorption, the bond length of N-O (1.181 Å) is slightly elongated compared to that in the free NO molecule (1.171 Å) indicating the weakening of the N-O bond due to molecular adsorption. Figure 4a compares the DOS of the NO molecule and Fe(B) atoms before and after NO adsorption. For an isolated NO molecule, as indicated in top panel of Fig. 4a, the sharp peaks correspond to 4σ, 1π, 5σ and 2π* orbitals. After adsorption, each molecular orbital is split into two because of the tilting of the adsorption geometry. An obvious broadening of the molecular orbitals can be observed due to the molecule-substrate interaction and molecule-molecule interaction. Compared to the clean surface, peaks located at approximately −12 eV in the local DOS of the Fe(B) atom (inset of 4th panel of Fig. 4a) are induced by the 4σ orbital of the adsorbed NO molecule. A similar process of electron donation also occurs at around -8 to -5 eV due to the 1π/5σ orbital of the adsorbed NO molecule. Different with the NO-adsorbed surface, the Fe(B) atom at the top/bottom most layer of clean surface has no contribution to the spin-down minimum conduction band. This makes the gap in the DOS of clean surface Fe(B) atom (bottom panel of Fig.4) looks like wider than that in Fig.3(a).

The free NO molecule has an unpaired electron in its 2π* orbital (top panel of Fig. 4a). After adsorption, there are considerable spin-down electronic states available over a wide energy range from -1.0 to E_F (2nd and 3rd panels of Fig.4a) which should be very helpful to spin injection into nonmagnetic materials. A NO molecule can either

View Article Online
DOI: 10.1039/C8CP02361A

donate its 2π* electron to the substrate or accept electron density from the substrate into the half-filled 2π* orbital. To visualize how the charge flows, differential charge densities for spin-down electronic states ($\Delta n_{\downarrow}$) are calculated at the energy range of -1.0 to E_F (Fig. 4b). $\Delta n_{\downarrow}$ is obtained by subtracting the spin-down electron densities of the isolated adsorbate $n(NO)_{\downarrow}$ and the clean substrate $n(Fe_3O_4)_{\downarrow}$ from that of the adsorbate/substrate system $n(NO/Fe_3O_4)_{\downarrow}$:

$$\Delta n_{\downarrow} = n(NO/Fe_3O_4)_{\downarrow} - n\left(Fe_3O_4\right)_{\downarrow} - n\left(NO\right)_{\downarrow}.$$

The latter two have the same geometric structure as the adsorbed system and the yellow or blue color indicates the gain or loss of electrons, respectively. Fig. 4b shows an obvious electron redistribution at the surface Fe(B) atoms and electron back donation to the adsorbed NO molecule. The electron redistribution can also be observed at the N atoms of NO molecules. The yellow color completely surrounding O atoms clearly provides evidence for the gain of electrons, namely the filling of the 2π* orbital of NO molecules. This well explains the enhancement of the magnetic moment of O atoms compared to the free NO molecule.

The spin polarization close to the Fermi level at the surface of a material is significant for its application in spintronic devices. The P_{EF} of clean Fe_3O_4(100) is known to be considerably reduced by the spin-up SSB states.[2-5] Figure 5 shows the spin density ($\Delta n = n_{\uparrow} - n_{\downarrow}$) of the NO-adsorbed Fe_3O_4(100) surface. The yellow or blue color indicates a positive or negative spin density, respectively. At energies very close to the Fermi level (-0.2 eV ~E_F; Fig. 5a), not only adsorbed NO molecules but also all surface atoms show a negative spin density although this very sparse for

View Article Online
DOI: 10.1039/C8CP02361A

surface atoms. When the energy range is enlarged from -0.5 eV to E_F (Fig. 5b), the adsorbates and Fe(B) atoms still show a significant negative spin density. The spin density is negative along the *z* direction of O2 atoms but positive at O1 atoms and in the *xy*-plane of O2 atoms. It is noticeable that the adsorbed NO molecules protrude toward the vacuum side with tilted geometries. Therefore, the positive spin density at surface O atoms might be partially shielded by the adsorbate. Consequently, the surface spin polarization is expected to be highly enhanced by the adsorption of NO molecules. Such a prediction could be confirmed through experimental measurements using spin-polarized electron spectroscopies.

IV. Conclusion

We have presented an investigation of the adsorption of NO molecules on an $Fe_3O_4(100)$ surface using both GGA and GGA+U methods. NO approaches the surface via its N atom and preferentially bonds with a surface Fe(B) atom. GGA is not recommended to be used in such a strongly correlated system since it provides not only an overestimation of the adsorption energy and an underestimation of the Fe(B)-N bond length, but also a magnetic quench of the adsorbate and the bonded Fe(B) atoms. Through the GGA+U method, a tilted adsorption geometry is obtained. The spin-up surface state bands are shifted to a deeper level and electrons are back-donated to the spin-down $2\pi^*$ orbital of the adsorbed NO molecule, resulting in an increase of the magnetic moment of the O atom and an enhancement of the surface spin polarization. The high density of spin-down states over a wide energy range (-1.0 eV to E_F) of the adsorbed NO molecules should help spin injection into nonmagnetic

View Article Online
DOI: 10.1039/C8CP02361A

materials.

Acknowledgment

This work was supported by the National Natural Science Foundation of China under Grant Nos. 11674297, 11274284 and U1632273. The numerical calculations in this paper were performed on the supercomputing system in the Supercomputing Center of University of Science and Technology of China and National Institute for Materials Science of Japan.

References

[1]Z. Zhang, S. Satpathy, *Phys. Rev. B* 1991, **44**, 13319.

[2]M. Fonin, R. Pentcheva, Y. S. Dedkov, M. Sperlich, D. V. Vyalikh, M. Scheffler, U. Rüdiger, and G. Güntherodt, *Phys. Rev. B* 2005, **72**, 104436.

[3]J. G. Tobin, S. A. Morton, S. W. Yu, G. D. Waddill, I. K. Schuller, and S. A. Chambers, *J. Phys.: Condens. Matter* 2007, **19**, 315218.

[4]M. Kurahashi, X. Sun and Y. Yamauchi, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2010, **81**, 193402.

[5]A. Pratt, M. Kurahashi, X. Sun and Y. Yamauchi, *J. Phys. D: Appl. Phys.* 2011, **44**, 064010.

[6]X. Sun, M. Kurahashi, A. Pratt and Y. Yamauchi, *Surf. Sci.* 2011, **605**, 1067.

[7]R. Pentcheva, W. Moritz, J. Rundgren, S. Frank, D. Schrupp and M. Scheffler, *Surf. Sci.* 2008, **602**, 1299.

View Article Online
DOI: 10.1039/C8CP02361A

[8]G. S. Parkinson, N. Mulakaluri, Y. Losovyj, P. Jacobson, R. Pentcheva and U. Diebold, *Phys. Rev. B: Condens. Matter. Mater. Phys.* 2010, **82**, 125413.

[9]X. Sun, S. D. Li, B. Wang, M. Kurahashi, A. Pratt, Y. Yamauchi, *Phys. Chem. Chem. Phys.* 2014, **16**, 95.

[10]X. Sun, A. Pratt, Y. Yamauchi, *Phys. Chem. Chem. Phys.* 2015, **17**, 15386.

[11]G.Kresse and J.Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 1996, **54**, 11169.

[12]G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* 1996, **6**, 15.

[13]J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.

[14]G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 1999, **59**, 1758.

[15]P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 1994, **50**, 17953.

[16]V.I. Anisimov, J. Zaanen, O.K. Andersen, *Phys. Rev. B,* 1991, **44**, 943.

[17]H. J. Monkhorst, J. D. Pack, *Phys. Rev. B: Solid State,* 1976, **13**, 5188.

[18]I. V. Shvets, G. Mariotto, K. Jordan, N. Berdunov, R. Kantor and S. Murphy, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2004, **70**, 155406.

[19]Z. Lodziana, *Phys. Rev. Lett.* 2007, **99**, 206402.

[20]R. Pentcheva, F. Wendler, H. L. Meyerheim, W. Moritz, N. Jedrecy and M. Scheffler, *Phys. Rev. Lett.* 2005, **94**, 126101.

[21]C. Cheng, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2005, **71**, 052401.

[22]Z. Jiang, W. Zhang, W. Shangguan, X. Wu and Y. Teraoka, *J. Phys. Chem. C,* 2011, **115**, 13035.

View Article Online
DOI: 10.1039/C8CP02361A

[23]C. Xiang, H. Tan, J. Lu, L. Yu, P. Song, C. Zeng, D. Zhang and S. Tao, *Phys. Scr.* 2014, **89**, 075401.

[24]A. Rohrbach and J. Hafner, *Phys, Rev. B*, 2005, **71**, 045405.

[25]H. Kuhlenbeck, G. Odörfer, R. Jaeger, G. Illing, M. Menges, Th. Mull, H. J. Freund, M. Pöhlchen, V. Stämmler, S. Witzel, C. Scharfschwerdt, K. Wennemann, T. Liedtke, and M. Neumann, *Phys. Rev. B,* 1991, **43**, 1969.

[26]R. Lindsay, P. Baumgärtel, R. Terborg, O. Schaff, A. M. Bradshaw, and D. P. Woodruff, *Surf. Sci.,* 1999, **425**, L401.

[27]J. T. Hoeft, M. Kittel, M. Polcik, R. L. Toomes, J. H. Kang, D. P. Woodruff, M. Pascal, and C. L. A. Lamont, *Phys. Rev. Lett.*, 2001, **87**, 086101.

[28]M. Kittel, J. T. Hoeft, S. Bao, M. Polcik, R. L. Toomes, J. H. Kang, D. P. Woodruff, M. Pascal, and C. L. A. Lamont, *Surf. Sci.* 2002, **499**,1.

[29]R. Wichtendahl, M. Rodriguez-Rodrigo, U. Härtel, H. Kuhlenbeck, and H.-J. Freund, *Surf. Sci.* 1999, **423**, 90.

[30] Z. Y. Li, M. Jibran, X. Sun, A. Pratt, B. Wang, Y. Yamauchi, Z.J. Ding, *Chem. Phys. Lett.* 2017, **675**, 15.

View Article Online
DOI: 10.1039/C8CP02361A

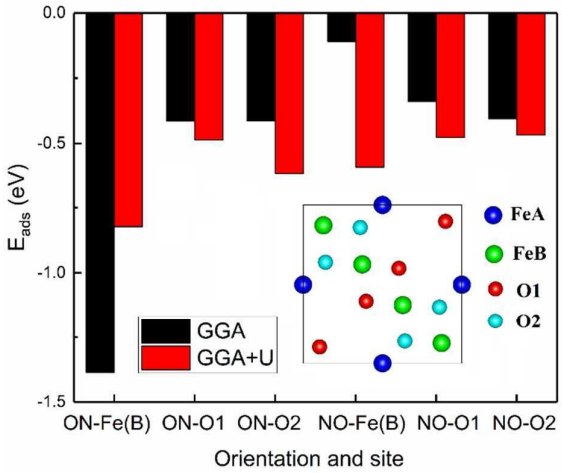

Figure 1. The adsorption energy of a NO molecule at different sites and orientations on the $Fe_3O_4(100)$ surface calculated using the GGA and GGA+U methods. Atoms of the top two layers of the Fe(B)-terminated $Fe_3O_4(100)$ surface are shown in the inserted figure with different colors.

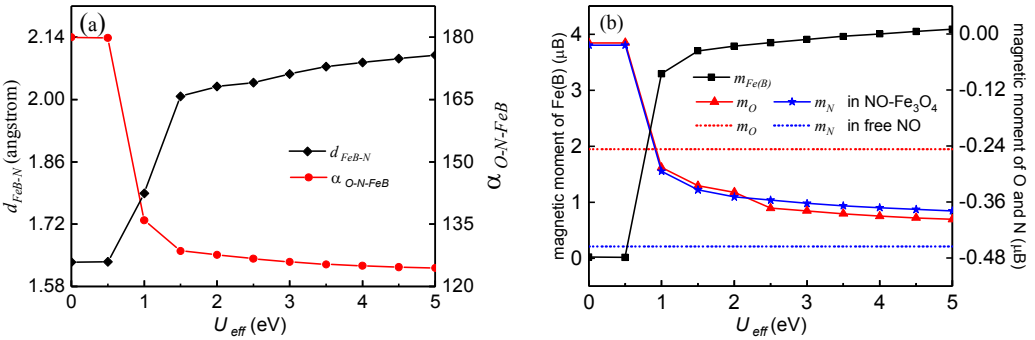

Figure 2. (a) The U_{eff} dependence of the Fe(B)-N bond length and the angle of the O-N-Fe(B) bonds. (b) The U_{eff} dependence of the magnetic moment of Fe(B), O, and N after NO adsorption. The horizontal dotted lines represent values of the magnetic moment of O and N atoms in free NO.

View Article Online
DOI: 10.1039/C8CP02361A

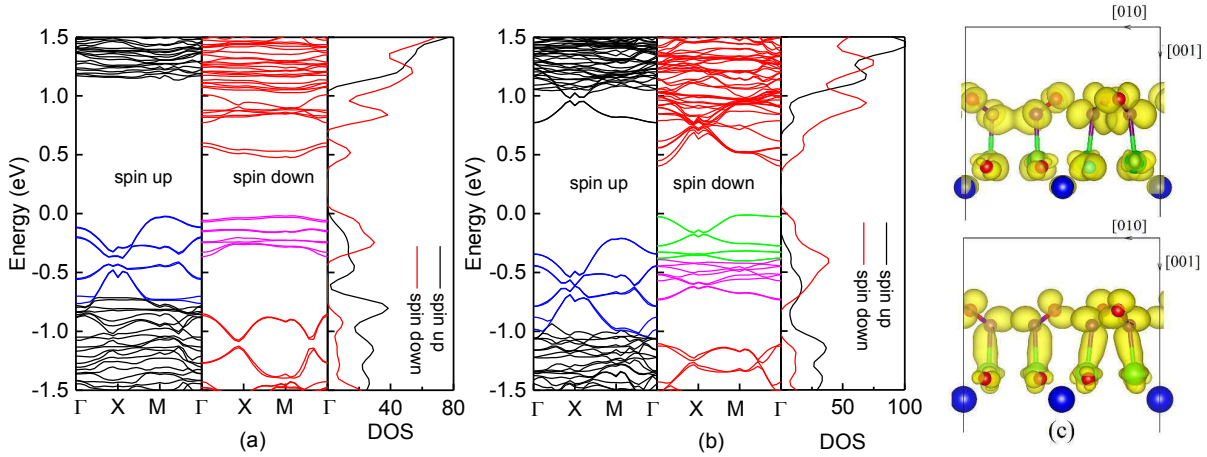

Figure 3. The band structure and total DOS of (a) clean $Fe_3O_4(100)$ and (b) NO-adsorbed $Fe_3O_4(100)$ surfaces calculated using GGA+U. (c) The isosurface (0.002 eV/Å^3) of the charge density of the spin-down bands plotted with green lines in the middle panel of (b)

View Article Online
DOI: 10.1039/C8CP02361A

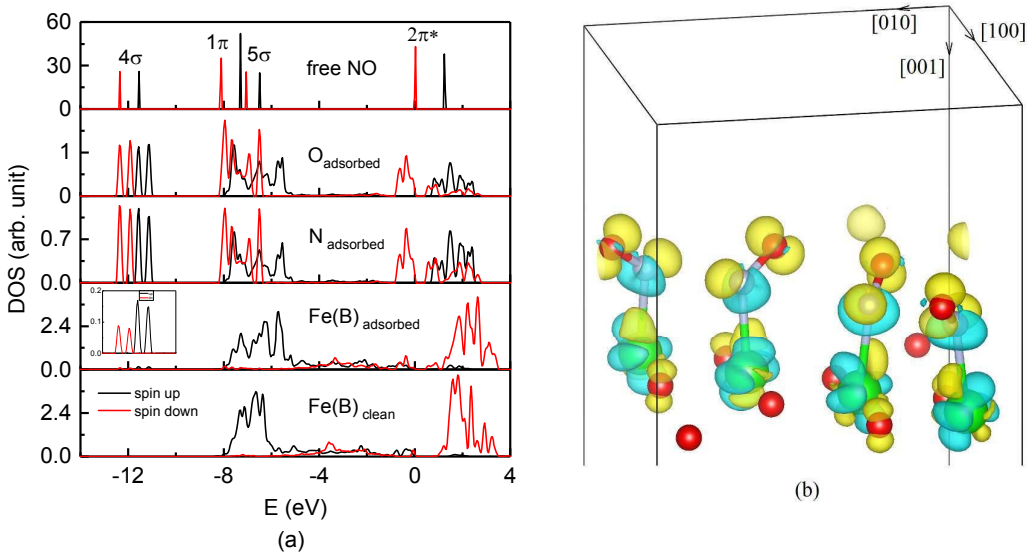

Figure 4 (a) DOS of a free NO molecule, the O and N atoms after NO adsorption, and the surface Fe(B) atom before and after NO adsorption. (b) Differential charge density for spin-down electronic states of a NO-adsorbed $Fe_3O_4(100)$ surface for the energy range of -1.0 eV to E_F. The yellow or blue color indicates the gain or loss of electrons respectively. The isosurface is plotted with 0.005 eV/Å^3.

View Article Online
DOI: 10.1039/C8CP02361A

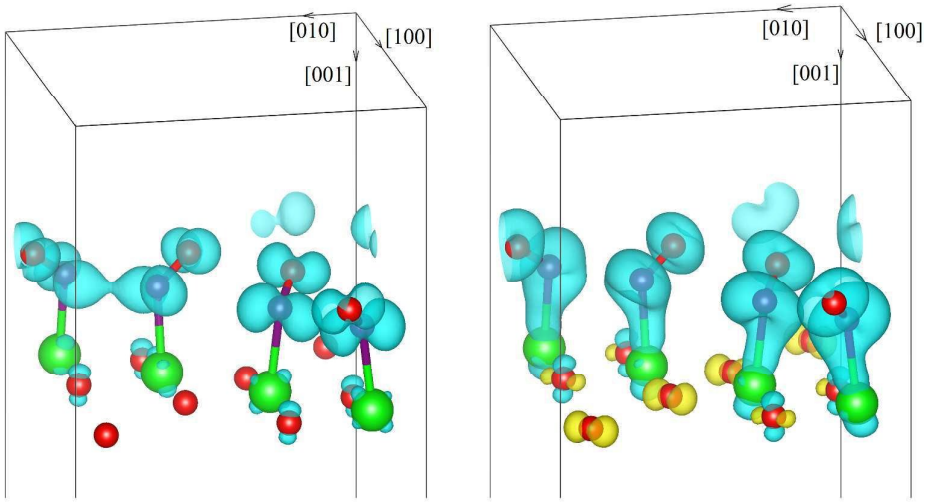

Figure 5 The spin density of NO-adsorbed Fe_3O_4(100) for an energy range of (a) -0.2 to E_F and (b) -0.5 to E_F. The yellow or blue color indicates positive and negative spin density with respective isosurfaces plotted with 0.002 and 0.006 eV/Å^3. Only the adsorbed NO molecules and atoms at the topmost surface are shown.